DETERMINATION OF LOW CONCENTRATIONS OF METHANE IN COAL-MINE-AIR SAMPLES BY INFRARED ABSORPTION SPECTROMETRY

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DETERMINATION OF LOW CONCENTRATIONS OF METHANE IN COAL-MINE-AIR SAMPLES BY INFRARED ABSORPTION SPECTROMETRY[1]

by

P. J. Colbassani[2] and H. A. Watson[3]

INTRODUCTION

Samples of mine atmospheres collected by Federal coal-mine inspectors during their inspections and investigations of coal mines, in accordance with provisions of the Federal Coal Mine Safety Act (66 Stat. 692; 30 U. S. C., secs. 451-483) are analyzed routinely by chemical methods at Bureau of Mines laboratories. When samples collected in open workings of nongassy coal mines at points not less than 12 inches from the roof, face, or rib contain 0.25 percent or more methane, the act requires the operator, during operation of such mine, to comply with the provisions of sec. 209, Title II, of the act, which pertain to gassy mines. The methane contents of such samples are determined by a physical method based on infrared absorption spectrometry to provide an independent check on analytical results obtained by chemical methods. This information circular describes the equipment and procedures used by the Bureau for determining low concentrations of methane in coal mine atmospheres by infrared absorption spectrometry.

ACKNOWLEDGMENTS

The authors are indebted to Dr. R. A. Friedel, Chief of Spectrometric Section, Branch of Coal-to-Oil Research, Bureau of Mines, for suggesting the analytical method and for furnishing valuable advice and assistance, and to J. A. Queiser of his staff for making exploratory measurements by this method; to Dr. M. G. Zabetakis of the Division of Explosives Technology for his assistance during the conduct of preliminary experimentation; and to L. B. Berger, Chief, Branch of Health Research, under whose guidance the equipment was procured and the work conducted.

DESCRIPTION OF METHOD

Principle

Methane absorbs radiation in the infrared region of the spectrum and can be identified by its characteristic absorption pattern. In coal-mine-air samples methane may be determined quantitatively by measuring the proportion of energy absorbed at a wavelength of 7.66 microns, where it exhibits its strongest absorption.[4] Since the energy absorbed, expressed as "optical density" or "absorbance," does not increase linearly with methane concentration, an empirical calibration curve made with accurately known concentrations of methane in air is used to evaluate the absorption data obtained during analysis of an unknown sample. The absorbance measurements during calibration and analytical procedures are made at the same preselected total gas pressure in a gas cell and under the same instrumental conditions.

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[1] Work on manuscript completed December 1957.

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[3] Chief, Gas Analysis and Research Section, Branch of Health Research, Bureau of Mines, Pittsburgh, Pa.

[4] Friedel, R. A., Spectrometric Investigations of Atmospheric Pollution: Anal. Chem., vol. 28, 1956, pp. 1806-1810.

The theory and application of these principles to the analysis of methane-containing gases have been described by McGovern[5] and others.[6-12]

Apparatus

The infrared instrument used in this work is a commercially built, dispersion-type, recording, double-beam spectrophotometer utilizing the optical null principle. Its function is to supply an infrared absorption spectrum of a sample by irradiating it and measuring the infrared radiation transmitted at successive frequencies over a selected wavelength region. The instrument and accessories are shown in figure 1.

A Nernst glower, which consists of an electrically heated column of rare-earth oxides, furnishes a source of radiant energy. By means of suitable optical components, radiation from this source is separated into 2 beams, 1 of which passes through a cell containing the gas sample to be examined; the other bypasses the cell to serve as a "reference" beam. A multiple-wedge type of diaphragm in the reference beam is movable into or out of the beam so that the intensities of the two beams may be brought to a balance or "null" point. The two beams then are combined by a rotating sector mirror that alternately transmits one beam (reference beam) and reflects the other (sample beam) in the same direction as the transmitted beam. The composite beam passes through a monochromator to a thermocouple-type detector. If the two beams are equal in intensity, no output is observed from the detector. If an infrared-absorptive gas is present in the cell the intensities of the two beams become unequal, and a pulsating voltage is generated by the detector. This electrical effect, after being amplified electronically, actuates a motor to move the diaphragm device into the reference beam to reduce its intensity enough to reestablish the balance. A pen coupled to the diaphragm mechanism continuously records the balance point on a chart on a rotating drum, thus furnishing a permanent record of the

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[5] McGovern, J. J., Spectrometric Analysis of Methane: Seminar talk pres. at Mellon Institute, Pittsburgh, Pa., October 1945.

[6] Coggeshall, N. D., and Saier, Eleanor L., Analyses of Mixtures of Light Gases by Infrared Absorption: Jour. Appl. Phys., vol. 17, 1946, pp. 450-456.

[7] Seyfried, W. D., and Hastings, S. H., Short-Cut Methods of Infrared Analysis: Anal. Chem., vol. 19, 1947, pp. 298-304.

[8] Delsemme, A. H., (Infrared Spectrographic Determination of Trace Components in Gases): Congr. groupement avance. méthod. anal. spectrograph. produits mét., vol. 12, 1949, pp. 125-127.

[9] Stroupe, J. D., Infrared Analysis of Certain C_1-C_4 Hydrocarbon Mixtures: Anal. Chem., vol. 22, 1950, pp. 1125-1128.

[10] Mellon, M. G., Analytical Absorption Spectroscopy: John Wiley & Sons, Inc., New York, N. Y., 1950.

[11] Barthauer, G. L., Haggerty, Alice, and Friedrich, R. J., Analysis of Synthesis Gas: Anal. Chem., vol. 25, 1953, pp. 256-259.

[12] Montigny, Pierre, Beer's Law in Infrared Spectrometry. Apparatus-Error Corrections and Analytical Applications: Congr. groupement avance, méthod. anal. spectrograph. produits mét., vol. 16, 1953, pp. 57-77.

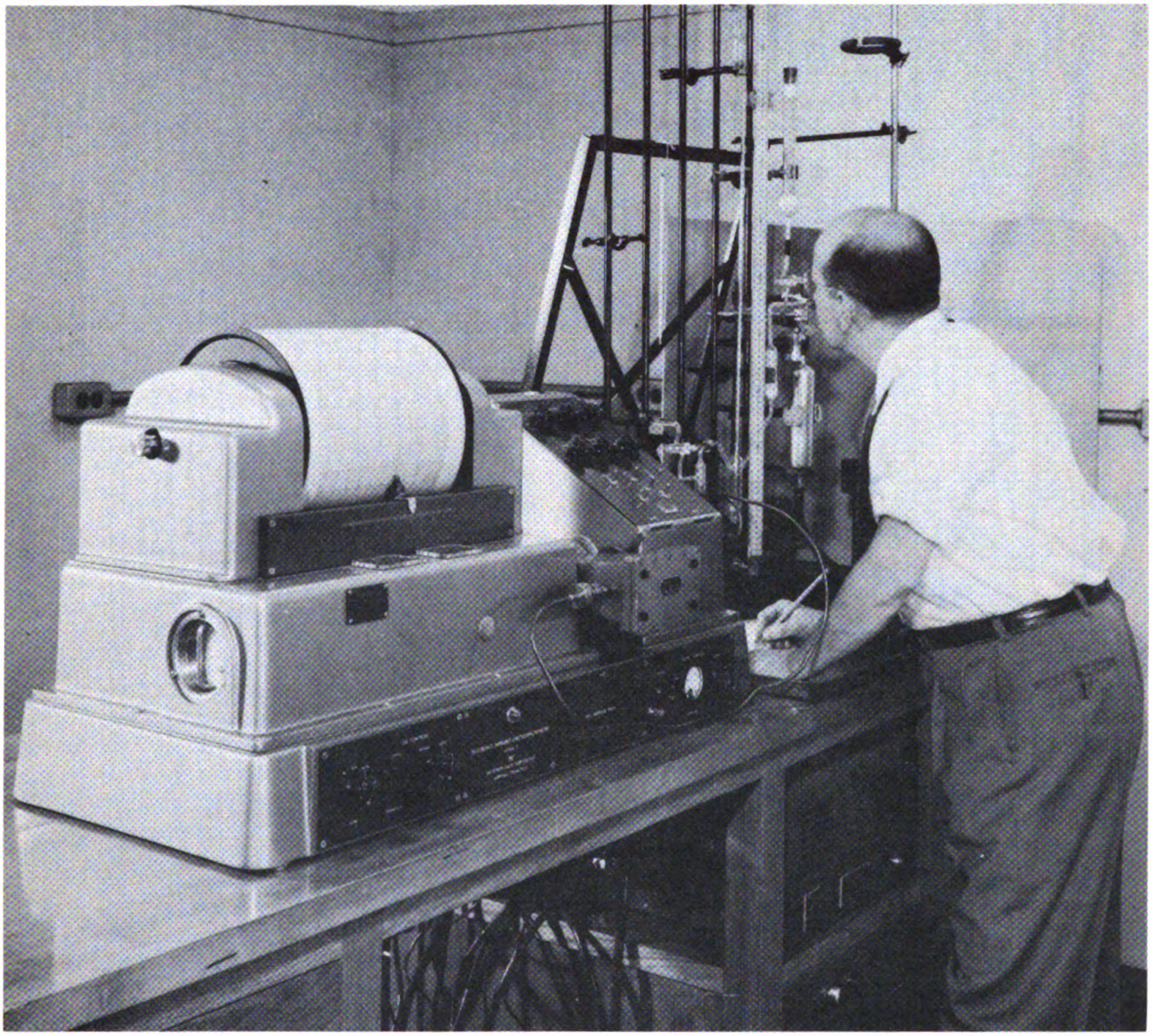


FIGURE 1. - Double-Beam, Dispersion-Type, Recording Infrared Spectrophotometer.

infrared energy transmitted by the sample. Figures 2 and 3 show spectra of air, and air containing carbon monoxide, methane, and ethane, respectively.

The monochromator is an optical system consisting of prism, mirrors, and slits to disperse the composite beam so that radiation of only a narrow range of frequencies reaches the infrared-sensitive detector at a given time during the wavelength region traversed. The effective frequency or wavelength of the radiation reaching the detector depends on the position of the prism and the width of the slit openings; it may be altered by rotating the prism, which is accomplished, in effect, by rotating a mirror behind the prism and by varying the slit widths.

The instrument is designed so that the wavelength range may be traversed at various controlled speeds and with various slit openings. Slit- and wavelength-controlling mechanisms and recorder chart drum are actuated by electric motors. After the instrument has been adjusted for a selected program of wavelength scanning speed and slit openings, the operation of producing a spectral chart for a sample becomes

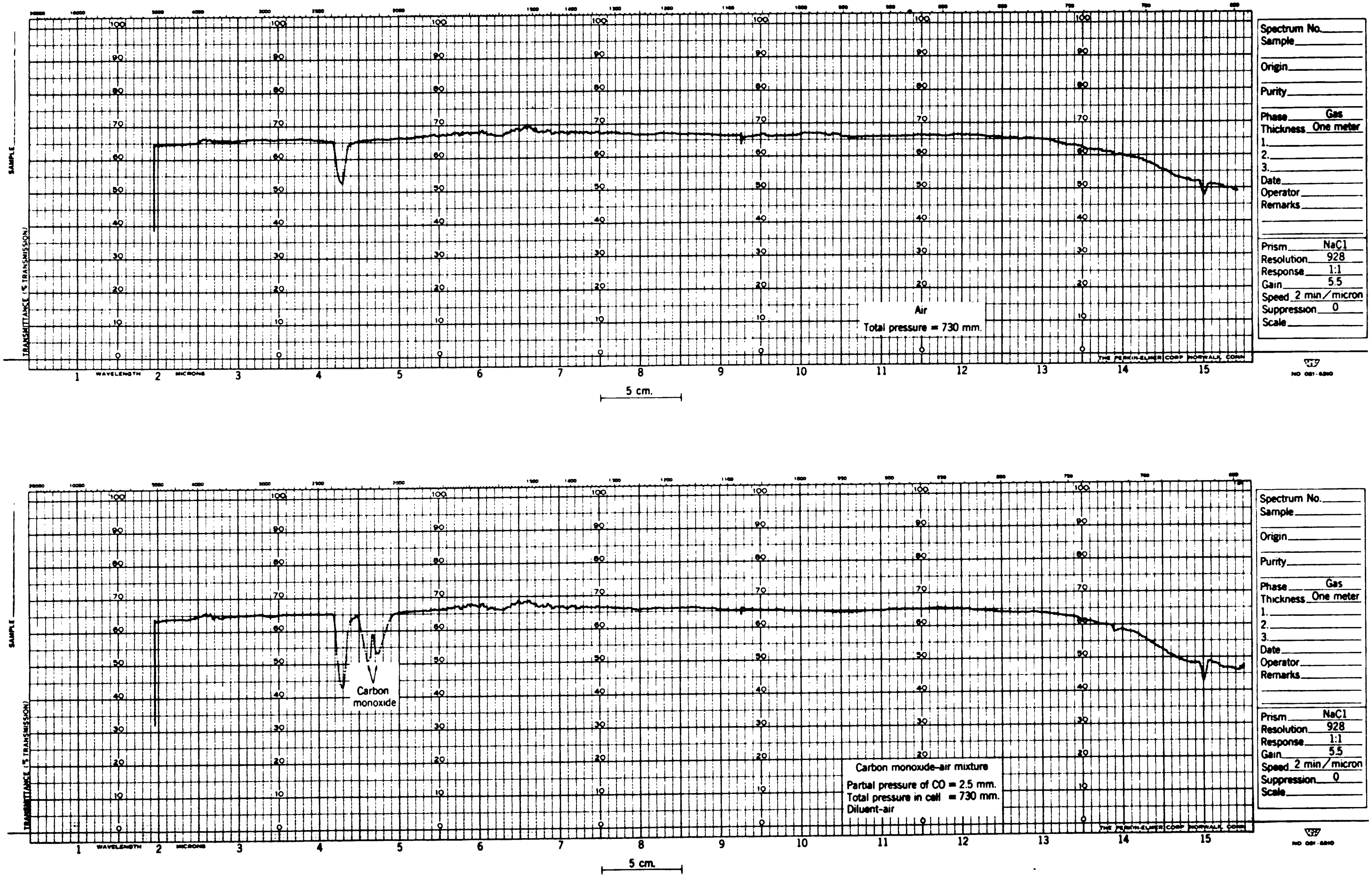
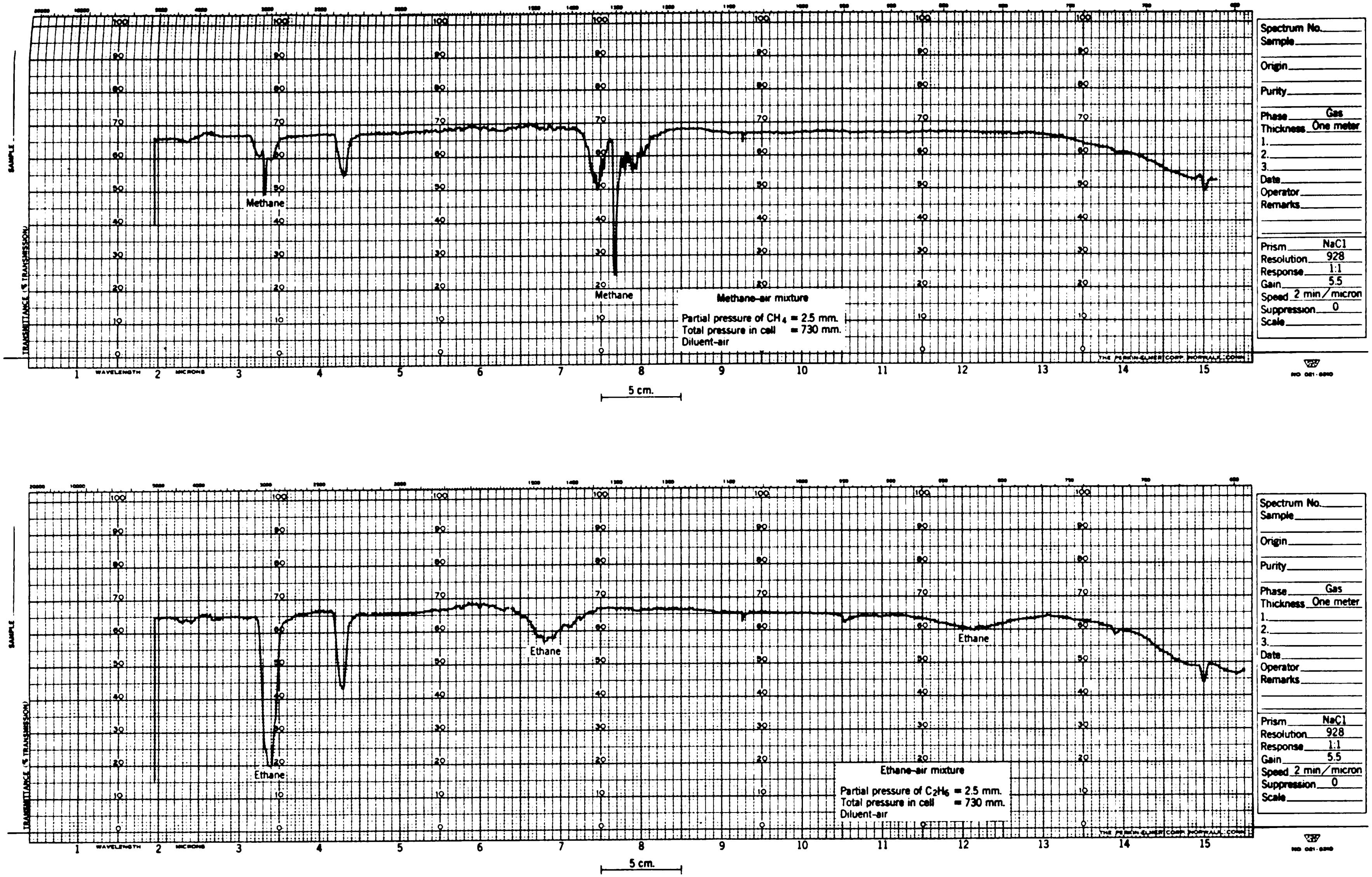


FIGURE 2. - Infrared Spectra of Air and of a Carbon Monoxide-Air Mixture.



Spectrum No.
Sample
Origin
Purity
Phase Gas
Thickness One meter
1.
2.
3.
Date
Operator
Remarks
Prism NaCl
Resolution 928
Response 1:1
Gain 5.5
Speed 2 min/micron
Suppression 0
Scale

FIGURE 3. - Infrared Spectra of Methane-Air and Ethane-Air Mixtures.

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automatic. The width of slit openings and wavelength values are shown continuously on indicators during the recording of a spectrum.

The spectrophotometer is equipped with a sodium chloride prism. The gas cell, which is fitted with potassium bromide windows, has an optical path length of 1 meter and a volume of approximately 950 milliliters. With these prism and window materials the useful wavelength range extends from 2 to 15 microns.

The gas sample to be examined is drawn from its container and introduced into the evacuated gas cell by means of a simple transfer device consisting of a mercury-filled reservoir with an attached leveling bottle. Gas pressures in the cell are measured with a mercury-filled closed-end manometer.

Calibration

An empirical calibration curve relating absorbance measurements to partial pressures of methane in the sample cell is prepared using standard mixtures containing known concentrations of methane in air. The calibration procedure follows:

(1) A portion of calibration mixture is introduced into the evacuated gas cell and the gas pressure (P_1) measured, enabling the partial pressure of methane to be calculated:

$$\text{Partial pressure of } CH_4 = \frac{CH_4\text{, percent by volume}}{100} \times P_1 \text{ (mm. Hg).}$$

(2) Air is introduced into the cell until a total gas pressure (P_2) of 730 millimeters of mercury is attained.

(3) Four successive infrared absorption spectra for the 6- to 9-micron wavelength range are recorded at a scanning speed of approximately 4 minutes per micron and a fixed slit opening of 0.066 millimeter, as shown on the slit-opening indicator. Corresponding "zero" lines, representing complete absorption of infrared radiation, are traced after an opaque shutter is placed in the sample beam.

These spectra for quantitative measurement of methane are recorded with the chart drum rotating at a rate of speed twice that for which the chart paper is calibrated. This does not affect the wavelength scanning rate but merely expands the spectrum longitudinally with respect to the printed wavelength scale to facilitate defining the tips of the absorption peaks.

(4) The absorption of infrared radiation by methane at the 7.66-micron peak is evaluated from the 4 spectral tracings by the "base-line" technique.13 14/ Figure 4 illustrates the manner in which the base-line absorbance is determined from a recorded spectrum. A straight line (baseline) is drawn between spectral points at 7.1 and 8.3 microns on the tracing. The distance between the base line and the zero line, representing the radiation (I_0) transmitted when methane is not present in the sample, is measured. The distance between the zero line and the tip of the absorption peak, representing the reduced radiation (I) transmitted when methane is present, is

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13/ Wright, N., Application of Infrared Spectroscopy to Industrial Research: Ind. Eng. Chem., Anal. Ed., vol. 13, 1941, pp. 1-8.

14/ Heigl, J. J., Bell, M. F., and White, J. V., Application of Infrared Spectroscopy to the Analysis of Liquid Hydrocarbons: Anal. Chem., vol. 19, 1947, pp. 293-298.

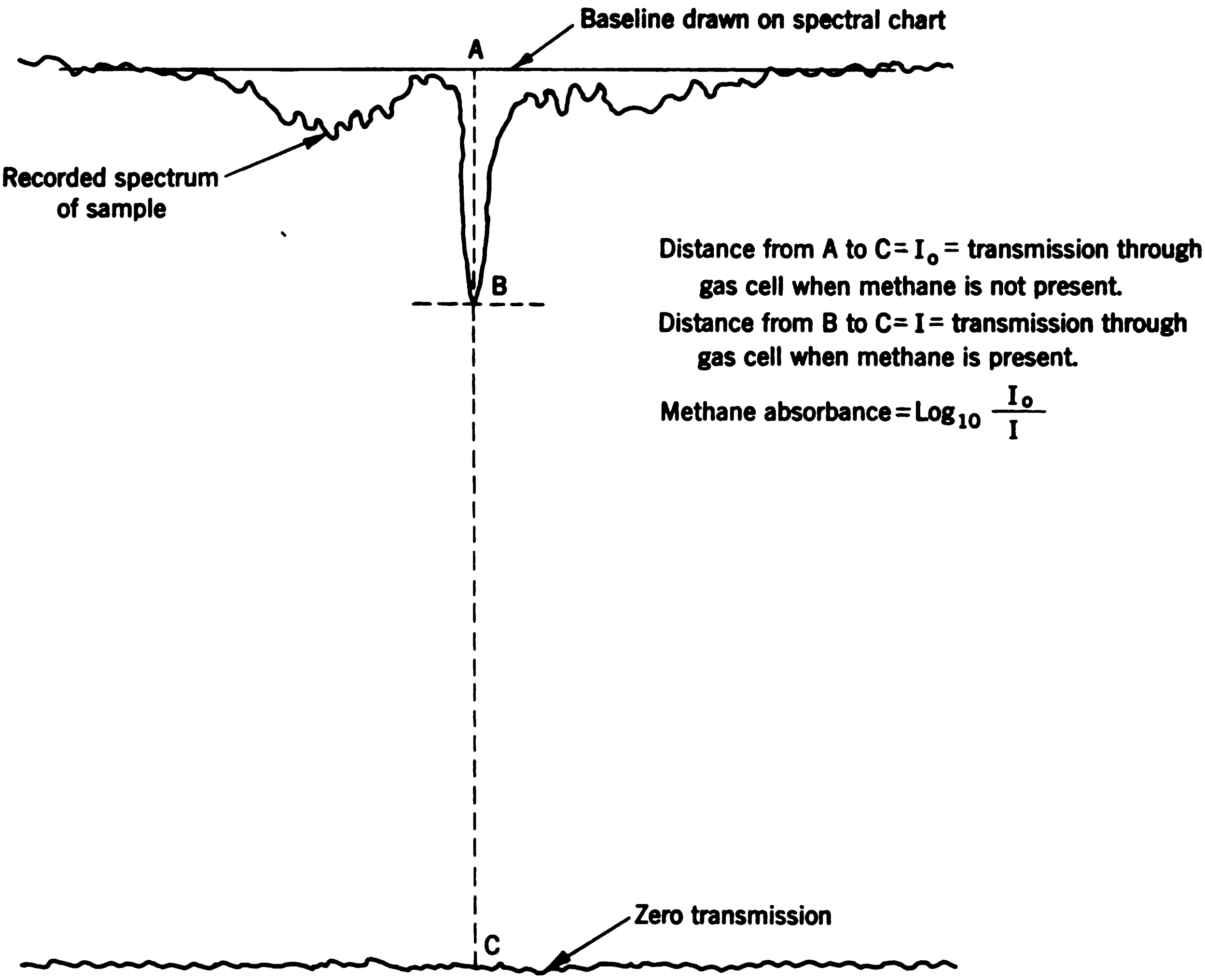
Baseline drawn on spectral chart
A
Recorded spectrum of sample
B
Distance from A to C = I_0 = transmission through gas cell when methane is not present.
Distance from B to C = I = transmission through gas cell when methane is present.
Methane absorbance = $\mathrm{Log}_{10} \frac{I_0}{I}$
Zero transmission
C

FIGURE 4. - Determination of Absorbance of Methane by Baseline Method.

similarly measured. From these two distances, measured at the same wavelength on the chart, the base-line absorbance is computed:

$$\text{Absorbance} = \mathrm{Log}_{10} \frac{I_o}{I}.$$

Since four spectral tracings are made, the I_o/I ratio is determined for each and the absorbance calculated from the average I_o/I value.

(5) A calibration curve in which partial pressure of methane is plotted versus base-line absorbance is constructed from data obtained thus under identical experimental conditions with several mixtures containing known concentrations of methane.

The representative calibration curve shown as figure 5 was based on 12 calibration points obtained with 6 calibration mixtures. In the present application the calibration range has been limited to a maximum partial pressure of methane of 1 millimeter of mercury. The range may be extended to higher partial pressures of methane if desired.

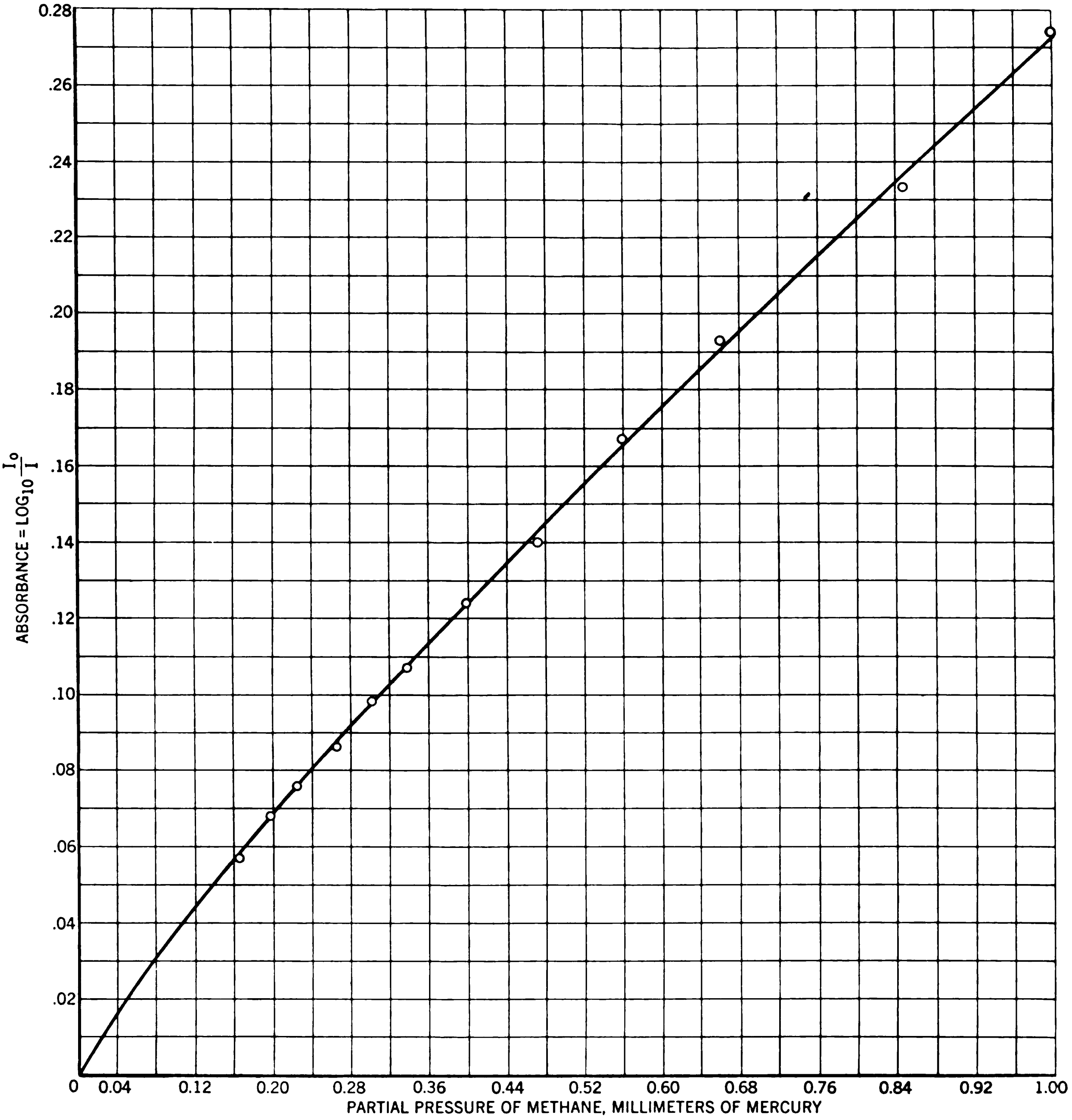

FIGURE 5. - Calibration Curve for Determining Low Concentrations of Methane in Mine Atmospheres.

Determination of Methane in Air Sample

The procedure for determining the methane content of an air sample is similar to that described under "Calibration." The sample is drawn into the evacuated cell and its pressure (P_1) measured. Air is introduced until a total pressure of 730 millimeters of mercury is attained. Four spectra are recorded for the 6- to 9-micron wavelength range, using the same scanning speed and slit openings as in calibration. Corresponding zero transmission lines also are recorded. I_o and I values are measured on each spectrum, the I_o/I ratio calculated and averaged, and the base-line absorbance computed:

$$\text{Absorbance} = \text{Log}_{10} \frac{I_o}{I} \text{ average.}$$

The partial pressure of methane equivalent to the calculated absorbance is read from the calibration curve. The concentration of methane in the sample, then, is calculated:

$$\text{Methane, percent by volume} = \frac{\text{Partial pressure of } CH_4}{P_1} \times 100.$$

PROCESSING SAMPLES FOR INFRARED ANALYSIS

During inspections by Bureau of Mines personnel, samples of mine atmospheres are collected in evacuated bottles of 200 to 250 milliliters capacity and analyzed in the laboratory by gas volumetric-combustion methods[15] for contents of carbon dioxide, oxygen, and methane. Carbon monoxide determinations, if required, are made by volumetric or colorimetric chemical methods, depending on the concentration encountered.

When it has been found, by volumetric-combustion analysis, that the methane content of a sample collected in a nongassy mine is 0.25 volume-percent or greater, no further analyses are made by this method, as it is desirable to conserve as much sample as possible for carbon monoxide determination and infrared examination.

Before infrared analysis approximately 50 milliliters of the air sample is withdrawn and analyzed for carbon monoxide content by a colorimetric procedure.[16] The combustion analysis is corrected for carbon monoxide, if present. An alternative procedure is to make the carbon monoxide determination in sample withdrawn from the infrared gas cell following that analysis. This procedure has the advantage that a larger volume of the original sample is available for the infrared analysis but has the disadvantage that the carbon monoxide determination must be made after the original sample has been diluted with several volumes of air.

The remaining sample is transferred to the infrared gas cell, its pressure (P_1) measured, and air added until a total gas pressure of 730 millimeters of mercury is attained in the cell. P_1 values obtained usually fall in the range of 90 to 130 millimeters of mercury. A spectrum for the 2- to 15-micron-wavelength range is prepared for record purposes and for qualitative examination. The quantitative determination of methane then is made as described under "Determination of Methane in Air Sample." Four spectra are recorded for the 6- to 9-micron-wavelength range for measurement and evaluation of energy absorption by methane at 7.66 microns.

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[15] Watson, H. A., and Berger, L. B., Equipment for Analyzing Mine Atmospheres, With Special Reference to Haldane-Type Apparatus: Bureau of Mines Inf. Circ. 7728, 1956, 51 pp.

[16] Polis, B. D., Berger, L. B., and Schrenk, H. H., Colorimetric Determination of Low Concentrations of Carbon Monoxide by Use of a Palladium Chloride-Phosphomolybdic Acid-Acetone Reagent: Bureau of Mines Rept. of Investigations 3785, 1944, 13 pp.

The mine-air sample is pumped from the gas cell and the cell flushed several times with air. The cell is reevacuated and a certified mixture[17] containing 0.26 ±.01 percent by volume of methane in air is introduced into the cell in sufficient amount to establish the same P_1 pressure value that was used in analyzing the subject mine-air sample. Air is added until a total pressure of 730 millimeters is attained. Four spectra of the certified mixture are recorded for the 6- to 9-micron-wavelength range with the same instrumental conditions used in analyzing the mine-air sample. Two of these spectra are recorded on the same chart bearing the latter two spectra of the mine-air sample, permitting direct comparison of absorption peaks of the known mixture with those of the mine-air sample. Even without evaluating absorption peaks in terms of methane by use of a calibration curve, these recorded spectra immediately furnish a visual means for determining whether or not the methane content of the mine-air sample is greater or less than 0.25 percent.

The measurement and evaluation of the absorption peaks in terms of methane concentration are made for the sample and the certified mixture following the procedure described in this circular.

Figures 6 and 7 show spectra obtained during analysis of an air sample from a coal mine. The pressure of sample introduced into the evacuated cell was 100 millimeters of mercury (P_1). Air was added to produce a total gas pressure of 730 millimeters in the cell (P_2). Figure 6 shows one 2- to 15-micron tracings and two 6- to 9-micron tracings of the coal-mine-air sample. Figure 7 shows two 6- to 9-micron tracings of the coal-mine-air sample, upon which 2 tracings of the standard methane-air mixture have been superimposed for comparison. Figure 7 also shows, on a separate chart, two additional 6- to 9-micron tracings of the standard methane-air mixture.

The analytical data and results are summarized as follows:

	I_o,[1] mm.	I,[1] mm.	I_o/I	$\log_{10} I_o/I$	Partial pressure of CH_4,[2] mm. Hg	Concentration of CH_4,[3] percent by volume
Coal-mine-air sample	137.0	108.5	1.263			
	137.7	109.4	1.259			
	137.0	109.2	1.255			
	136.5	107.9	1.265			
	Average		1.26	0.100	0.314	0.31
Standard methane-air mixture	137.0	111.8	1.225			
	136.5	112.8	1.210			
	137.5	112.8	1.219			
	137.2	113.4	1.210			
	Average		1.22	.086	.263	.26

[1] Measured on 6- to 9-micron spectral tracings.

[2] Read from calibration curve.

[3] Calculated from CH_4, percent = $\frac{\text{Partial pressure of } CH_4}{P_1} \times 100$.

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[17] Prepared and certified by National Bureau of Standards, U. S. Department of Commerce, Washington, D. C.

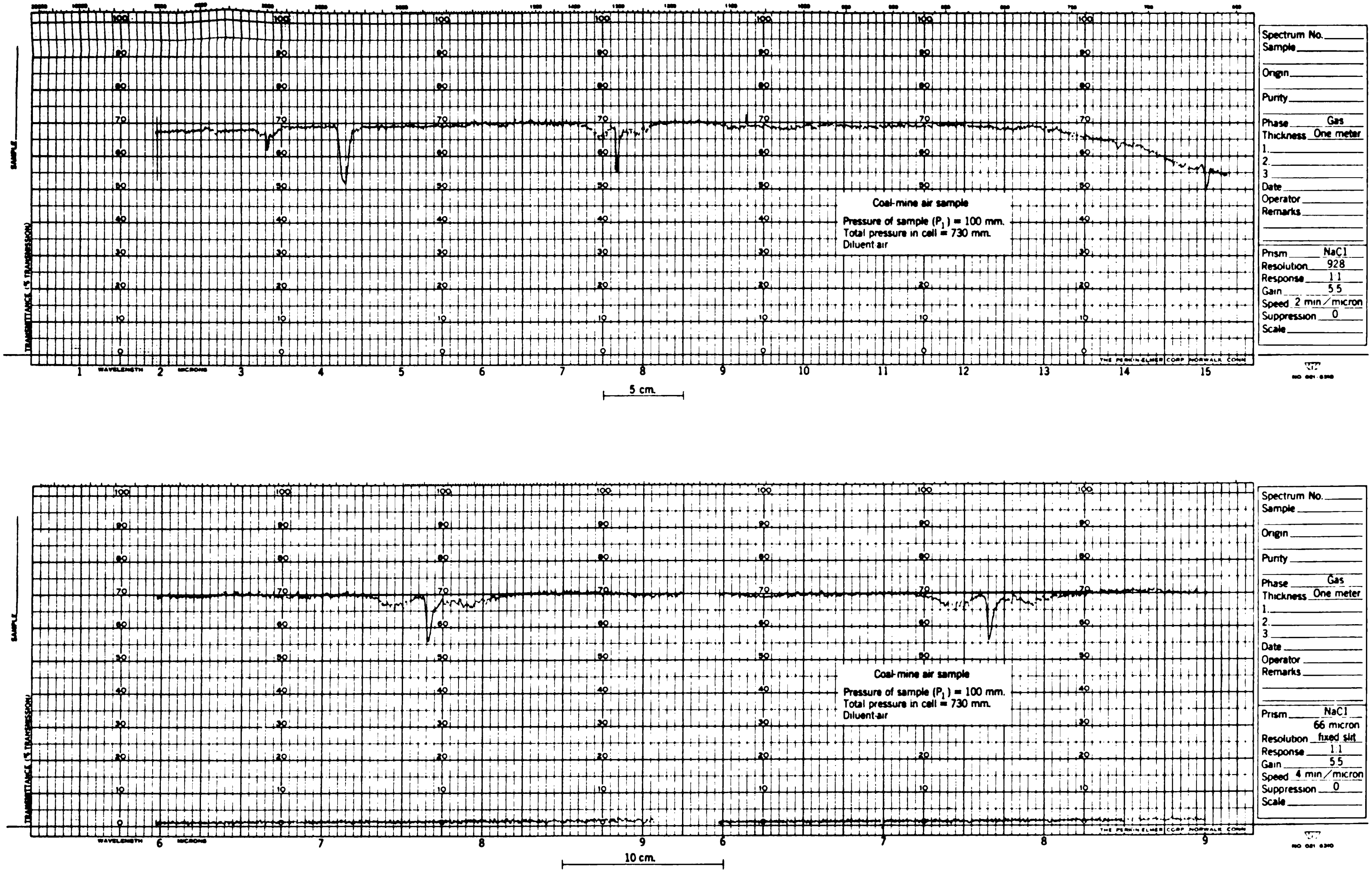

FIGURE 6. - Infrared Spectra of a Coal-Mine-Air Sample.

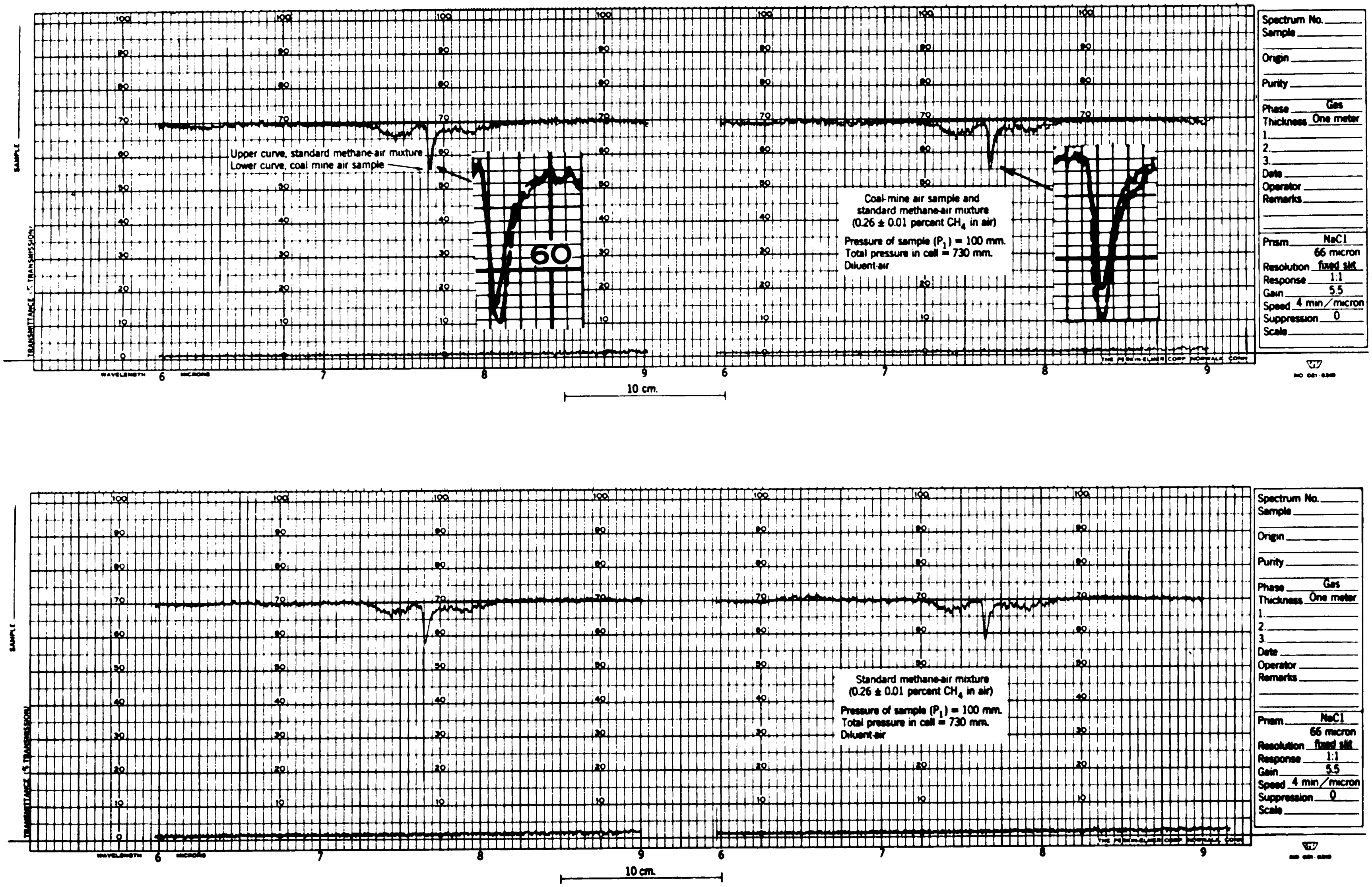

FIGURE 7. - Infrared Spectra of a Coal-Mine-Air Sample and a Standard Methane-Air Mixture.

DISCUSSION

Infrared absorption spectrometry permits methane to be determined without interference from low concentrations of ethane and carbon monoxide that may be present in coal-mine-air samples. This is evident from figures 2 and 3, which show four spectra - of dry air and of air mixtures, respectively, of carbon monoxide, methane, and ethane - over the wavelength range of 2 to 15 microns. The partial pressure of the added gas (carbon monoxide, methane, or ethane) was approximately 2.5 millimeters of mercury, which, in the P_1 sample pressure range (90 to 130 millimeters) normally obtained with the mine-air-sample volumes available for analysis, represents volume concentrations of the order of 1.9 to 2.8 percent. Air was added as a diluent to produce a total gas pressure of 730 millimeters in the cell.

The principal regions of absorption are indicated on the spectra for the added gases. The approximate positions (wavelengths) at which the absorption maxima occur are:

	Microns
Carbon monoxide	4.6 and 4.7
Methane	3.3 and 7.7
Ethane	3.4, 6.8, and 12.2

Absorption peaks common to all of these spectra at approximately 4.3, 13.9, and 15.0 microns are those of carbon dioxide. Nitrogen and oxygen do not exhibit infrared absorption peaks. The shape of the methane absorption spectrum in the neighborhood of the 7.66-micron peak, with its associated "fine structure," is characteristic of this gas and serves as a reliable means for its identification.

The accuracy of the determination of methane at the concentration point of particular interest (0.25 percent, by volume) may be estimated from results of repetitive analyses of the certified comparison standard mixture containing 0.26 ±.01 percent of methane. Over a period of 2 years this mixture was analyzed 28 times, with the following distribution of values:

Methane, percent by volume	Frequency
0.23	1
.24	1
.25	7
.26	10
.27	9

The maximum value obtained was 0.01 percent high; the minimum value was 0.03 percent low. Approximately 90 percent of the values varied not more than ±0.01 percent.

CONCLUSIONS

Infrared absorption spectrometry may be used under the conditions described to identify and determine methane accurately without interference from low concentrations of other gases that might be present in coal-mine air.

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